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The role of acidity in crystallization of lactose and templating approach for highly-porous lactose production

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ABSTRACT

This study has investigated the effect of different concentrations for various templating acids on the porosity of the final products from a new templating approach. A new production process has been successfully developed to create highly-porous powder templates through the spray drying of lactose solutions containing ethanol-soluble food-grade acids as templating agents and then removing these acids by ethanol washing of the spray-dried powders. The extents of in-process crystallization for the lactose/templating acids powders have been studied during spray drying. It has been found that increasing the templating-acids concentrations significantly increased the degrees of crystallinity for lactose in spray-dried powders. Textural properties, such as the surface area of the resultant lactose, changed considerably by varying the concentrations of different templating acids, due to changes in the degrees of lactose crystallinity for the final spray-dried products. The yields from spray drying have also been significantly decreased at higher concentrations of templating acids.

1. Introduction

Production of stable and high-porosity lactose particles has applications in the food industry and in drug delivery for pharmaceutical applications. In our previous works (Ebrahimi et al., 2015; Saffari et al., 2015), a new spray drying and post-processing technique based on a templating concept has been developed to create highly-porous organic powders. Templating techniques have been extensively used to produce highly-porous particles with multi-component mixtures of inorganic and colloidal materials (Emmanuelawati et al., 2013; Fiorilli et a., 2013; Nandiyanto et al., 2013; Sinha and Sidhu, 2012).

In this technique, the core materials, and the food-grade acid as the templating agent (both water soluble), have been mixed and spray dried. The resulting amorphous powders have been washed with ethanol to create porous powder particles by removing the ethanol-soluble acid and to simultaneously crystallize the powder, giving stable porous and crystalline powder particles. Novel contributions of the new process reported in this work include the use of a food-grade, non-toxic and benign templating material, citric acid, in a process involving spray drying, which is a low-cost continuous drying technique relative to many other drying operations, such as freeze drying. It has been found that altering the concentration of citric acid as a templating material could be very effective in changing the degrees of lactose crystallinity in the spray-dried products and the BET surface areas of the resultant porous materials. The results of our study suggested that there may be a link between the extent of lactose crystallization in the spray-dried powders and the BET surface areas for the ethanol-washed particles. That is, increasing the degree of crystallinity for the spray-dried powders at high citric acid concentrations decreased the amounts of citric acid molecules incorporated in the lactose structure, leading to lower BET surface areas (Ebrahimi et al., 2015).

Due to the importance of lactose in the food and pharmaceutical industries, there have been extensive studies on the crystallization behavior of lactose (Jouppila et al., 1998; Roos and Karel, 1992). It has been suggested that the crystallization rates of various amorphous sugars can be estimated by using the Williams–Landel–Ferry (WLF) equation (Williams et al., 1955). The ratio (r) of the time for crystallization (θ_{cr}) at any temperature (T) to the time for crystallization (θ_g) at the glass-transition temperature (T_g) can be correlated by the Williams–Landel–Ferry (WLF) equation, Eq. (1) (Williams et al., 1955). The WLF equation can be expressed as a rate equation (Eq. (2)) for the crystallization process by assuming that the crystallization rate is inversely proportional to the crystallization time:

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$$\log_{10} r = \log_{10}\left(\frac{\theta_{cr}}{\theta_g}\right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (1)$$

$$\frac{k_{cr}}{k_g} = 10^\wedge\left[\frac{-17.44(T - T_g)}{51.6 + (T - T_g)}\right] \quad (2)$$

where θ_{cr} is the time for crystallization (s), θ_g is the time for crystallization at the glass-transition temperature (s), k_{cr} is the rate of crystallization (s^{-1}) at the particular local conditions ($T-T_g$), and k_g is the rate of crystallization (s^{-1}) at the glass-transition temperature (T_g). The glass-transition temperature, which is specific for each material (Roos and Karel, 1991), can be estimated from the Gordon–Taylor equation (1952). The glass-transition temperature is affected by various factors, of which the composition of the material, the molecular weight and the water (moisture) content are the most important. According to the Williams–Landel–Ferry (WLF) equation, a higher particle temperature and lower particle glass-transition temperature increase the crystallization rate of the particles during the spray-drying process.

Saffari et al. (2015) and Bhandari (2008) found that significant increases in the degrees of crystallinity for the final spray-dried products of lactose solutions have occurred at increasing lactic acid concentrations, and the yields from spray drying have also been significantly decreased at higher concentrations of lactic acid. They reported that this increase in crystallinity may be due to increasing the $T-T_g$ difference (with the low T_g of lactic acid) and consequently decreasing the crystallization time, according to the Gordon–Taylor and Williams–Landel–Ferry equations. The increase in the rate of lactose crystallization at low pH may also be connected with the increase in the mutarotation rate and the rate of orientation of lactose molecules into the crystals (Jenness, 1988; Nickerson and Moore, 1974; Saffari et al., 2015; Singh et al., 1991).

The effect of glass-transition temperature and strength of the acid (pH of the solution) on the degree of crystallinity for lactose in spray-dried powders is critical, with implications for the performance of the templating approach using acidic templates. Therefore, the aim of this research is to investigate the effect of using different concentrations for various food-grade acids, such as lactic acid, citric acid, boric acid, and ascorbic acid, on the degree of crystallinity for spray-dried lactose powders and the porosity of the ethanol-washed powders. A templating approach has been applied here according to the method described in our previous works (Ebrahimi et al., 2015; Saffari et al., 2015). The results of this study have implications in choosing the best processing conditions to control the extent of lactose crystallization for producing spray-dried powders with high concentrations of surface asperities and large specific surface areas in order to increase the dissolution rates of food products such as food infusions and also in flavoring or encapsulating processes.

2. Materials and methods

2.1. Sample preparation

In these experiments, the following materials have been used: pure α-lactose monohydrate crystals ($C_{12}H_{22}O_{11}{\cdot}H_2O$; analytical reagent, Australia), citric acid as monohydrate ($C_6H_8O_7{\cdot}H_2O$; analytical reagent from Chem-Supply, Australia), lactic acid 88% w/w ($C_3H_6O_3$; laboratory reagent from Chem-Supply, Australia), ascorbic acid ($C_6H_8O_6$; analytical reagent from Chem-Supply, Australia), boric acid (H_3BO_3; laboratory reagent from Ajax Finechem, Australia), and whey protein isolate (Balance, Vitaco Health Ltd, Auckland, New Zealand, consisting of 92 g protein, 0.4 g fat (total) including 0.2 g saturated fat, 0.5 g carbohydrate, and sodium 0.6 g per 100 g).

In order to investigate and report the effects of different templating acid concentrations on the BET surface areas of lactose, experiments were carried out by varying the composition of the solutions with different amounts of templating acids (citric acid, ascorbic acid, boric acid, and lactic acid), whilst maintaining the level of lactose concentration in solution at 10% (w/w). Each solution was made up to a total weight of 100 g. A magnetic stirrer was used to enhance the dissolution rate of lactose at the room temperature of 25 °C for at least 30 min, so that clear solutions were obtained without any visible crystals being present. The clear solutions were then spray dried. The pH of the solutions was measured with a pH electrode, InPro 3250 series (Mettler Toledo, M 300, Switzerland). Further experimentation has been done by adding whey protein isolate (0.2%, w/w) to 10% (w/w) lactose solutions to increase the yield of the process (Islam et al., 2013) and also by controlling the degree of crystallinity and varying the compositions of the solutions with different additions of templating acids.

2.2. Operating conditions for spray drying

A Buchi B-290 spray dryer has been used in the experiments. The inlet air temperature has been 180 °C, the main air flow rate through the dryer has been 38 m^3/h (aspirator setting of 100%), the pump rate has been 8 mL/min (25% of the maximum rate), and the nozzle air flow rate has been 470 L/h (40 on the nozzle rotameter scale). Freshly spray-dried powder was collected from a collection vessel at the bottom of a cyclone and was immediately used for analytical tests (moisture content, modulated differential scanning calorimetry (MDSC), and gravimetric moisture analysis); otherwise, the powders were kept in sealed bags and in a refrigerator for X-ray diffraction and scanning electron microscope (SEM) tests on the following day. Part of the powder collected from the vessel at the bottom of the cyclone has been washed with ethanol for 48 h at the room temperature of 25 °C to remove the templating acid, filtered under vacuum, and dried for one hour in a laboratory oven at 60 °C. Crushing, grinding, and sieving the dried powder mass was used to produce the final powders. For each concentration, experiments have been done three times, and at least two replicate analyses have been done on samples. Data in this study have been presented as means ± STD (standard deviation) and were obtained from at least three independent experiments. Fig. 1 illustrates the overall process.

2.3. Powder characterization

2.3.1. Moisture sorption and oven drying tests

Time-dependent moisture sorption tests have been carried out for the powders from each experiment. It has been suggested that the moisture adsorption peak heights (changes in moisture content, percent ($100 \times$ kg kg^{-1} dry basis)) from the moisture-sorption experiments can be used to investigate the extent of lactose amorphicity by detecting the mass change profile during the absorption of moisture and the subsequent desorption due to the crystallization taking place in the sample (Buckton and Darcy, 1996; Imtiaz-Ul-Islam and Langrish, 2008; Saffari and Langrish, 2014). The end of the crystallization process can be determined by the point where the sorption curve reaches a plateau region (Jouppila et al., 1998; Jouppila and Roos, 1994b; Lai and Schmidt, 1990). Amorphous materials absorb moisture more than their corresponding crystalline counterparts, and after the moisture-induced recrystallization, the desorption of excess water after crystallization of the amorphous components is observed (Lehto et al., 2006).

A mass of 1–2 g of the powder product obtained just after spray drying the sample solution was placed on a Petri dish (borosilicate glass) of 10-cm-diameter. The dish was placed in an analytical balance (±0.0001 g, Mettler Toledo, AB 204-S, Switzerland), and the